

4.2 Equilibrium of two liquid phases, critical solution temperature

Depending on temperature, two liquids may partially dissolve with each other, or may dissolve with each other without any restriction. A phase diagram regarding liquid phase-liquid phase equilibrium of water-phenol system is shown in Fig. 4.1. The graph shows the relationship between temperature and composition as pressure being constant (1 atm). Under the condition of constant pressure, one degree of freedom is excluded. Therefore, phase rule regarding a two component system is indicated $F' = 3 - P$. When only one liquid phase is present ($P = 1$), it is $F' = 2$. That is, temperature and composition can optionally be changed. When two liquid phases are co-present ($P = 2$), it is $F' = 1$. That is, where temperature is specified, composition of two liquid phases is determined. Further, where composition of one liquid phase is specified, composition of other liquid phase and temperature are determined. In the region designated $L_1 + L_2$ in Fig. 4.1, two liquid phases are co-present, and only one phase is present in a region outside such a region.

One point A is indicated within a two phase region, a horizontal line is drawn through A, and points crossing the line with two curves are indicated B and C. Line BC is a tie line. At this temperature, a system corresponding to the composition of point A is present dividing into two phases, and the

respective composition is given by points B and C. This shows mutual solubility of two liquids. Two liquid phases under equilibrium are called a conjugate solution. The relative amount of those is determined by "rule of lever" (see Item 3.2). Where temperature rises, the mutual solubility increases, the compositions of two conjugate solutions gradually approach, and ultimately those compositions coincide at the temperature of the maximum point M. At a temperature higher than this temperature, two liquids become to dissolve with each other without any restriction. Such a temperature is called a critical solution temperature. In detail, this is an upper consolute temperature (abbreviated as UCT).

As mentioned above, in the composition and temperature at the point A, the system is divided into two liquid phases. When the temperature rises, water-rich liquid phase increases, and phenol-rich liquid phase decreases. In addition, composition of each phase varies. When the temperature arrives at point D, the phenol-rich liquid phase disappears. At a temperature higher than that temperature, only one liquid phase is present. Reversely, when cooling, separation into two phases begins at the point D. When elevating the temperature of the system corresponding to the composition of the maximum point, the compositions of the co-present two liquid phases gradually approach. When reaching the critical solution temperature, the boundary surface of phases abruptly disappears,

and one liquid phase is formed.

In contrast with the above example, there is a system that two liquid phases dissolve with each other in any optional proportion at a certain temperature or lower. This temperature is called a lower consolute temperature (abbreviated as LCT). As the example, a temperature-composition diagram of water-dipropylamine system is shown in Fig. 4.2. In this system of this type, the mutual solubility of two liquids decreases with the rise of temperature. This is explained as follows. Because the amine and water form a weak complex at low temperature, the solubility is large. When elevating temperature, the complex is broken, and as result, the solubility decreases.

There is also a system having both the upper consolute temperature and the lower consolute temperature. As such an example, a temperature-composition diagram of water-nicotine system is shown in Fig. 4.3*. Two liquid phases are co-present in the region surrounded with the closed curve, and only one liquid phase is present in a region outside such a region. In this case, the mutual solubility of two liquid phases decreases with the rise of temperature, but at a certain temperature or higher, it reversely increases.

Examples of the system having the critical solution temperature are shown in Table 4.1.

Table 4.1 Two component system having critical solution temperature

Component A	Component B	Critical solution Temperature/°C		Weight percentage of B
Water	Phenol	UCT	66.4	33.4
Phenol	Hexane	UCT	52.6	52.2
Hexane	Methanol	UCT	42.6	31.1
Water	Diethylamine	LCT	143.5	37.4
Water	Dipropylamine	LCT	-4.8	33.7
Water	Triethylamine	LCT	18.5	36
Water	Nicotine	LCT	61	32.2
		UCT	210	32.2
Water	2,6-Dimethyl-	LCT	45.3	27.2
	Pyridine	UCT	164.9	33.8

Fig. 4.1

Temperature-composition diagram of water-phenol system

Fig. 4.2

Temperature-composition diagram of water-dipropylamine system

Fig. 4.3

Temperature-composition diagram of water-nicotine system

* In this case, because high temperature involves,

measurement is conducted in a sealed tube. Therefore, pressure of a system equals to vapor pressure, and varies depending on temperature. However, influence of pressure affecting liquid phase-liquid phase equilibrium is small.